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REVIEW ON DIFFUSION IN POLYMERS AND RUBBERS (U)

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1. INTRODUCTION

1.1 General

The important subject of diffusion in elastomers deals with the process by which matter is transported within the rubber sample. The absorption of larger quantities of liquids is undesirable as it may lead to weakening or disintegration of the rubber. Many technical applications of rubber are based on its property to slow down, or sometimes accelerate, diffusion of foreign molecules. For instance, Brintzinger [1949] proposed a method for the separation of the various organic compounds which utilizes permeation through a rubber membrane. Nowadays, membrane separation processes are used in several separation applications. Membrane permeation technology is discussed by several authors, e.g., Bemberis [1986] and Stooky et al. [1986].

To understand the aspects of diffusion, it is essential to consider also the solubility of the foreign molecules in rubber, i.e., the state of equilibrium between the molecules outside and inside the elastomer. In this state the polymer has taken up as many molecules by dissolution as is to be expected thermodynamically from the properties and concentrations of the polymer and the foreign substance. As long as equilibrium has not been reached the rubber continues to take up or give off foreign molecules and this involves transport by diffusion.

All experimental work on diffusion may be guided by the mathematical laws governing diffusion. These laws involve external variables (dimensions of the test piece, time) and the intrinsic properties of the system investigated. Intrinsic factors of the diffusion process include: temperature, concentration, dimensions of the diffusing molecules and physical and chemical properties of rubber. Diffusion can also provide an insight into the molecular structure and its relation to various physical properties [Ferry, 1970].

A special subject closely related to diffusion is permeation. This process is concerned with, the crossing by foreign molecules of a rubber membrane that separates two regions containing these foreign molecules at different concentrations or pressures. Today the membrane separation processes have growing applications in many industries. [Weber and Bowman, 1986].

In this preliminary report, the phenomenlogical theory of diffusion is presented. The mathematical formulation of desorption from a rectangular parallelopiped is given and the diffusion process in a permeation chamber is briefly discussed. Using the molecular network theory the effect of swelling in elastomers is studied. A method for calculating the diffusion coefficient from liquid lattice theory is presented and the basics of concentration dependent diffusion coefficients are briefly discussed.

2. REVIEW OF THE LITERATURE

2.1 General

It is known that relaxation processes are accompanied by "equilibration" in various physical quantities. These equilibration processes are manifested by macroscopic currents of mass, energy (heat), and electric charge. In the linear approximation, these processes can be described by a simple evolution equation - the diffusion equation. The form of this equation can be derived easily with the help of irreversible thermodynamics.

The diffusion equation contains one material function - the diffusion coefficient. Predicting the value of such a diffusion coefficient from molecular parameters is a difficult and important problem. The liquid-lattice theory can be used for predicting diffusion coefficients, however, the expression used for that purpose is very complicated. One can avoid that complicated form and resort to using various empirical and semi-empirical expressions which are reported in the literature, e.g., Crank [1975].

The properties of a rubber or a polymer sample affect to a large extent the diffusion in such samples. The basic mechanical properties of elastomers are discussed and the simple molecular network theory of rubbers is presented. Moreover, the effect of swelling is also discussed from the point of view of this theory. It should be noted that the diffusion processes can be used for the evaluation of some network parameters.

2.2 The Irreversible Thermodynamical Basis of the Diffusion Equation

If the state of thermodynamic equilibrium is disturbed then irreversible (relaxation) processes occur in the system. These processes will bring the system to a new equilibrium state. All relaxation processes are accompanied by "equilibration" in density, concentration, temperature and so on. These equilibration processes are associated with various macroscopic motions (currents or fluxes) inside the system, e.g., mass flux, flux of energy, electric current. The state of thermodynamic equilibrium is characterized by zero fluxes, i.e., all state parameters have constant values. Considering slow nonstatic processes we can divide the whole nonequilibrium system into a number of equilibrium macroscopic parts. Each of these parts is, at a given time, characterized by the constant temperature, density and concentration of its components. Particular parts of the system are in a state of internal equilibrium but, they are not at equilibrium with respect to the other parts. Here we are talking about a local equilibrium. In every moment there exist nonzero gradients of concentration, temperature, electric potential and other quantities. These gradients are associated with the transport of mass, energy and electric current during the nonstatic processes. If the gradients of macroscopic quantities are not too large, one can express the macroscopic currents as linear functions of these gradients. There exist a number of slow nonstatic processes where this condition is met, e.g., Ohm's law, Fourier's law of heat conduction, Fick's law of diffusion. These are examples of "pure"

effects which can be superposed (e.g., thermodiffusion or thermoelectric effects).

Consider a closed nonequilibrium system in which the slow nonstatic processes exist. Let λ_1, λ_2, ..., λ_n be differences of state parameters from their equilibrium values. Then λ_i characterizes the "degree of nonequilibrium" for a given system. (at equilibrium $\lambda_i = 0$ for all i).,

Since the entropy S is a function of parameters λ_i and $\lambda_i(t)$, we can write:

$$\dot{S} = \sum_i \frac{\partial S}{\partial \lambda_i} \dot{\lambda}_i \qquad (2.1)$$

where the dot represents the time derivative. The time change $-\dot{\lambda}_i$ is associated with the transport of some physical quantity (e.g., mass, energy, electric current, ..., etc.) and hence, it is called the i-th flux (current) - J_i. The derivative $-(\frac{\partial S}{\partial \lambda_i})$ represents a generalized thermodynamic force X_i (associated with parameter λ_i). Denoting:

$$-\dot{\lambda}_i = J_i \ , \ -\frac{\partial S}{\partial \lambda_i} = X_i \qquad (2.2)$$

then Equation (2.1) can be written as follows:

$$\dot{S} = \sum_i J_i X_i \qquad (2.3)$$

If the production of entropy is different in different parts of the system, one can write:

$$\dot{S} = \int \sum_i J_i X_i \, dV \qquad (2.4)$$

where $\sum_i J_i X_i$ represents the entropy production in a unit volume.

Assume that the quantities λ_i fully characterize the process of approaching equilibrium. Then, the rate of change of λ_i ($\dot{\lambda}_i = -J_i$) is the function of the parameters λ_i at the same time, i.e.

$$\dot{\lambda}_i = -J_i \equiv -J_i(\lambda_1, \lambda_2, \ldots, \lambda_n) \qquad (2.5)$$

For small departures from equilibrium ($\lambda_i \to 0$), one can use the linear approximation:

$$-\dot{\lambda}_i = J_i = \sum_k \alpha_{ik} \lambda_k \quad (i = 1,2, \ldots, n) \qquad (2.6)$$

where $\alpha_{ik} = \left(\frac{\partial J_i}{\partial \lambda_k}\right)_0$ are constant coefficients.

There are no terms of order zero, since for $\lambda_1 = \lambda_2 = \ldots = \lambda_n = 0$ all $\dot{\lambda}_i$ must be zero. At thermodynamic equilibrium all X_i's are zero and for small disturbances of equilibrium one can write:

$$X_i(\lambda_1, \ldots, \lambda_n) = -\sum_k \gamma_{ik} \lambda_k, \quad (i = 1,2, \ldots, n) \qquad (2.7)$$

where

$$\gamma_{ik} = -\left(\frac{\partial X_i}{\partial \lambda_k}\right)_0 = \left(\frac{\partial^2 S}{\partial \lambda_i \lambda_k}\right)_0$$

is a symmetric tensor ($\gamma_{ik} = \gamma_{ki}$). Solving Equation (2.7) with respect to $\lambda_i (= \lambda_i(X_1, \ldots, X_n))$ and substitution into Equation (2.6) one obtains:

$$\dot{\lambda}_i = -J_i = -\sum_k L_{ik} X_k, \quad (i = 1,2, \ldots, n). \qquad (2.8)$$

The quantities L_{ik} are kinetic coefficients. Onsager [1931] proved that the matrix L_{ik} is symmetric, i.e.

$$L_{ik} = L_{ki} \qquad (2.9)$$

Onsager's relations (2.9) relate the i-th component of flux to its k-th component. In phenomenological thermodynamics, one has to consider Onsager's relations as a new principle. The validity of this principle is there verified by its consequences [Prigogine, 1967].

Substituting Equation (2.8) into (2.3) or (2.4) one obtains the

following equations for the entropy production:

$$\dot{S} = \sum_{i,k} L_{ik} X_i X_k \qquad (2.10)$$

or

$$\dot{S} = \int \sum_{i,k} L_{ik} X_i X_k \, dV \qquad (2.11)$$

Since $\dot{S} > 0$, then the quadratic form in (2.10) (or (2.11)) must be definite positive, i.e.,

$$L_{11} > 0, \quad \begin{vmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{vmatrix} > 0, \ldots \qquad (2.12)$$

Application of the above formalism to diffusion is in order.

Consider an isolated isotropic system which as a whole is in a state of rest. Further assume that the system consists of two nonreacting components. The concentration of one component is C (the second component has concentration 1-C). During relaxation processes there exists the mass flux $\underset{\sim}{i}$ leading to the equilibration of concentration in different parts of the system. Moreover, there exists the heat flux, $\underset{\sim}{q}$, in the system. Let ρ be the total density (mass per unit volume) in a given volume element and u be the energy of a unit mass. The conservation of energy yields:

$$\frac{\partial}{\partial t} \int \rho\, u\, dV = \oint \underset{\sim}{q}\, d\underset{\sim}{\sigma} \tag{2.13}$$

or

$$\frac{\partial}{\partial t}(\rho u) = \rho \frac{\partial u}{\partial t} + u \frac{\partial \rho}{\partial t} = -\,\mathrm{div}\, \underset{\sim}{q} \tag{2.14}$$

where $\oint d\underset{\sim}{\sigma}$ represents the surface integral over dV.

Analogously, the conservation of mass can be written as:

$$\frac{\partial}{\partial t} \int \rho\, c\, dV = -\oint \underset{\sim}{i}\, d\underset{\sim}{\sigma} \tag{2.15}$$

or

$$\frac{\partial}{\partial t}(\rho c) = \rho \frac{\partial c}{\partial t} + c \frac{\partial \rho}{\partial t} = -\,\mathrm{div}\, \underset{\sim}{i} \tag{2.16}$$

Here, $\underset{\sim}{i}$ is the vector of the density flux for a given component (ρc is the mass of this component in a unit volume). For the entropy production we can write:

$$\dot{S} = \frac{\partial}{\partial t} \int \rho s\, dV = \int \left(s \frac{\partial \rho}{\partial t} + \rho \frac{\partial s}{\partial t}\right) dV \tag{2.17}$$

where s is the entropy per unit mass. Denote the number of particles of the given components as n_1 and n_2 and the masses of particles as m_1 and m_2, respectively. (Note that, $n_1 m_1 + n_2 m_2 = 1$). Then the thermodynamic equation for one gram of the mixture is:

$$du = Tds - Pdv + \mu_1 dn_1 + \mu_2 dn_2 \tag{2.18}$$

Here, v is the specific volume, P is the pressure, μ_1 and μ_2 are chemical potentials. With density $\rho = 1/v$ and concentration $c = n_1 m_1$, the last equation can be rewritten as:

$$du = Tds + \frac{P}{\rho^2} d\rho + \mu dc \tag{2.19}$$

where

$$\mu = \frac{\mu_1}{m_1} - \frac{\mu_2}{m_2} \tag{2.20}$$

Gibbs potential, g, for one gram of the mixture is given by the following equations:

$$g = u - Ts + \frac{P}{\rho} = \mu c \tag{2.21}$$

$$dg = -sdT + \frac{1}{\rho} dP + \mu dc \tag{2.22}$$

From Equation (2.19) it follows:

$$T \frac{\partial s}{\partial t} = \frac{\partial u}{\partial t} - \frac{P}{\rho^2} \frac{\partial \rho}{\partial t} - \mu \frac{\partial c}{\partial t} \qquad (2.23)$$

then

$$\frac{\partial}{\partial t} (\rho s) = \rho \frac{\partial u}{\partial t} - \frac{\mu \rho}{T} \frac{\partial c}{\partial t} - (s - \frac{P}{\rho T}) \frac{\partial \rho}{\partial T} \qquad (2.24)$$

With the help of Equations (2.14) and (2.16) the last equation yields:

$$\frac{\partial}{\partial t} (\rho s) = \frac{\mu}{T} \operatorname{div} \underset{\sim}{i} - \frac{1}{T} \operatorname{div} \underset{\sim}{q} - \frac{\rho}{T} [u - Ts + \frac{P}{\rho} - \mu c] \frac{\partial \rho}{\partial t}$$

and since $\mu c = u - Ts + \frac{P}{\rho}$ (viz. (2.21), we can write:

$$\frac{\partial}{\partial t} (\rho s) = \frac{\mu}{T} \operatorname{div} \underset{\sim}{i} - \frac{1}{T} \operatorname{div} \underset{\sim}{q} \qquad (2.25)$$

Using the identity:

$$\mu \operatorname{div} \underset{\sim}{i} - \operatorname{div} \underset{\sim}{q} = - \operatorname{div}(\underset{\sim}{q} - \mu \underset{\sim}{i}) - \underset{\sim}{i} \nabla \mu \qquad (2.26)$$

we can write the entropy production $\dot{S}$ as follows:

$$\dot{S} = \frac{\partial}{\partial t}\int \rho s \, dV = -\int \frac{1}{T} \operatorname{div}(\underset{\sim}{q} - \mu \underset{\sim}{i}) dV - \int \frac{\underset{\sim}{i}}{T} \underset{\sim}{\nabla} \mu \, dV \tag{2.27}$$

With the help of relations:

$$b \operatorname{div} \underset{\sim}{B} = -\underset{\sim}{B} \underset{\sim}{\nabla} b + \operatorname{div}(b\underset{\sim}{B}) \tag{2.28}$$

$$b = \frac{1}{T}, \; \underset{\sim}{\nabla} b = -\frac{1}{T^2} \underset{\sim}{\nabla} T, \; \underset{\sim}{B} = \underset{\sim}{q} - \mu \underset{\sim}{i}$$

and Gauss' theorem we can also write:

$$\dot{S} = -\int \frac{1}{T^2} (\underset{\sim}{q} - \mu \underset{\sim}{i}) \underset{\sim}{\nabla} T dV - \int \frac{\underset{\sim}{i}}{T} \underset{\sim}{\nabla} \mu \, dV - \oint \frac{1}{T} (\underset{\sim}{q} - \mu \underset{\sim}{i}) d\underset{\sim}{\sigma} \tag{2.29}$$

Then the energy flux is determined by $(\underset{\sim}{q} - \mu \underset{\sim}{i})$. If this flux is zero on the boundary of the system then:

$$\dot{S} = -\int \frac{1}{T^2} (q - \mu i) \nabla T \, dV - \int \frac{\underset{\sim}{i}}{T} \underset{\sim}{\nabla} \mu \, dV \tag{2.30}$$

and the entropy production is written in the form (2.4). The forces X_i are represented by components of vectors:

$$-\frac{\nabla T}{T^2} \quad \text{and} \quad -\frac{\nabla \mu}{T}$$

and the fluxes J_i are given as components of vectors:

$$(q - \mu i) \quad \text{and} \quad i$$

As we know from Equation (2.8), the fluxes J_i can be written as linear combinations of thermodynamic forces, i.e.:

$$i = -\alpha T\left(\frac{\nabla \mu}{T}\right) - \beta T^2\left(\frac{\nabla T}{T^2}\right) \tag{2.31}$$

$$q - \mu i = -\eta T\left(\frac{\nabla \mu}{T}\right) - \gamma T^2\left(\frac{\nabla T}{T^2}\right)$$

where $L_{11} = \alpha T$, $L_{12} = \beta T^2$, $L_{21} = \eta T$ and $L_{22} = \gamma T^2$.

Since $L_{12} = L_{21}$, then:

$$\eta = \beta T \tag{2.32}$$

and

$$i = -\alpha \nabla \mu - \beta \nabla T \tag{2.33}$$

$$\underset{\sim}{q} = -\beta T \underset{\sim}{\nabla} \mu - \tau \underset{\sim}{\nabla} T + \mu \underset{\sim}{i} \tag{2.34}$$

Eliminating $\underset{\sim}{\nabla} \mu$ from Equation (2.34) one can write:

$$\underset{\sim}{i} = -\alpha \underset{\sim}{\nabla} \mu - \beta \underset{\sim}{\nabla} T \tag{2.35}$$

$$\underset{\sim}{q} = (\mu + \frac{\beta}{\alpha} T)\underset{\sim}{i} - \kappa \underset{\sim}{\nabla} T$$

where $\kappa = \tau - \frac{\beta^2 T}{\alpha}$

Vector $\underset{\sim}{i}$ represents the total mass flux (diffusion current). For $\underset{\sim}{i} = 0$ then $\underset{\sim}{q} = -\kappa \underset{\sim}{\nabla} T$, here κ is the heat conductivity. Substituting Equations (2.35) into (2.30) one obtains:

$$\overset{\bullet}{S} = \int \frac{\kappa(\underset{\sim}{\nabla} T)^2}{T^2} dV + \int \frac{\underset{\sim}{i}^2}{\alpha T} dV \tag{2.36}$$

From the second thermodynamic theorem, it follows that:

$$\kappa > 0 \quad \text{and} \quad \alpha > 0 \tag{2.37}$$

For coefficient γ one has then:

$$\gamma > \frac{\beta^2 T}{\alpha} > 0 \qquad (2.38)$$

Since the chemical potential, μ, is a function of c, P and T, i.e., $\mu \equiv \mu(c,P,T)$, one obtains:

$$\underset{\sim}{\nabla}\mu = \left(\frac{\partial \mu}{\partial c}\right)_{P,T} \underset{\sim}{\nabla} c + \left(\frac{\partial \mu}{\partial P}\right)_{c,T} \underset{\sim}{\nabla} P + \left(\frac{\partial \mu}{\partial T}\right)_{c,P} \underset{\sim}{\nabla} T \qquad (2.39)$$

and from Equation (2.22) it follows that ($v = 1/\rho$)

$$\left(\frac{\partial \mu}{\partial P}\right)_{c,T} = \left(\frac{\partial v}{\partial c}\right)_{P,T} \qquad (2.40)$$

It is useful to introduce the following notation:

$$D = \frac{\alpha}{\rho}\left(\frac{\partial \mu}{\partial c}\right)_{P,T}, \quad \frac{\rho D \theta}{T} = \alpha\left(\frac{\partial \mu}{\partial T}\right)_{c,P} + \beta \qquad (2.41)$$

$$\frac{\rho D \pi}{P} = \alpha\left(\frac{\partial \mu}{\partial P}\right)_{c,T}$$

Using these notations in Equation (2.39) and substituting $\nabla\mu$ into the mass flux $\underset{\sim}{i}$ one obtains:

$$\underset{\sim}{i} = -\rho D(\underset{\sim}{\nabla} C + \frac{\theta}{T} \underset{\sim}{\nabla} T + \frac{\Pi}{P} \underset{\sim}{\nabla} P) \qquad (2.42)$$

and

$$\underset{\sim}{q} = [\theta \left(\frac{\partial \mu}{\partial c}\right)_{P,T} - T\left(\frac{\partial \mu}{\partial T}\right)_{c,P} + \mu]\underset{\sim}{i} - \kappa \underset{\sim}{\nabla} T \qquad (2.43)$$

It follows from Equation (2.42) that the mass flux $\underset{\sim}{i}$ consists of three terms:

$$\underset{\sim}{i}_c = -\rho D \underset{\sim}{\nabla} c, \quad \underset{\sim}{i}_T = -\frac{1}{T} \rho D_\theta \underset{\sim}{\nabla} T, \quad \underset{\sim}{i}_P = -\frac{1}{P} \rho D_\Pi \underset{\sim}{\nabla} P$$

and

$$\underset{\sim}{i} = \underset{\sim}{i}_c + \underset{\sim}{i}_T + \underset{\sim}{i}_P \qquad (2.44)$$

The flux $\underset{\sim}{i}_c$ corresponds to the regular diffusion, $\underset{\sim}{i}_T$ describes the thermodiffusion and $\underset{\sim}{i}_P$ is the barodiffusion. The corresponding coefficients are:

D - diffusion coefficient

D_θ - thermodiffusion coefficient

D_Π - barodiffusion coefficient

Usually, one can neglect $\underset{\sim}{\nabla} P$ with respect to $\underset{\sim}{\nabla} T$ and $\underset{\sim}{\nabla} c$. If $\underset{\sim}{\nabla} T$ and

$\underset{\sim}{v}c$ are small, then one can assume that D and θ are constants. Neglecting the term $c(\frac{\partial P}{\partial t})$ in Equation (2.16), one obtains:

$$\rho \frac{\partial c}{\partial t} + \text{div } \underset{\sim}{i} = 0 \tag{2.45}$$

With the help of Equation (2.42) this equation yields:

$$\frac{\partial c}{\partial t} = D(\Delta C + \frac{\theta}{T} \Delta T) \tag{2.46}$$

Similarly, neglecting the term $\underset{\sim}{i} \nabla \mu$ in Equations (2.25) and (2.26) one obtains:

$$\rho T \frac{\partial s}{\partial t} + \text{div}(\underset{\sim}{q} - \mu \underset{\sim}{i}) = 0 \tag{2.47}$$

Using Equation (2.23), the following equation for temperature is obtained:

$$\frac{\partial T}{\partial t} - \frac{\theta}{C_p} \left(\frac{\partial \mu}{\partial c} \right)_{P,T} \frac{\partial c}{\partial t} = \chi \Delta T \tag{2.48}$$

Here, C_p is the specific heat of one gram of the mixture and $\chi = \kappa/\rho C_p$ is the coefficient of thermometric conduction. For pure diffusion and heat conduction then one has the following two parabolic equations:

$$\frac{\partial c}{\partial t} = D \Delta C \quad \text{and} \quad \frac{\partial T}{\partial t} = \chi \Delta T \tag{2.49}$$

These two equations are thoroughly studied in monographs of Crank [1975]-diffusion equation, and Carslaw and Jaeger [1959]-heat equation.

2.3 Diffusion Coefficient from Liquid Lattice Theory

In 1935 Bethe developed a very ingenious method for dealing with configurational problems on super-lattices. He had been concerned with alloys, but it was realized that his method is applicable to configurational problems in the study of mixtures.

Flory [1942] and Huggins [1942] formulated the theory of polymeric solutions with the help of liquid lattice theory [Flory and Krigbaum, 1951]. In this theory the liquid and polymer molecules are considered to be arranged on a three-dimensional lattice of sites such that each site may be occupied either by a liquid molecule or by a single segment of a polymer chain. If the polymer molecule contains x segments and we have N-polymer molecules and n liquid molecules in the system, then the entropy of mixing (ΔS_m) is given as follows:

$$\Delta S_m = -k(n \ln v_1 + N \ln v_2) \tag{2.50}$$

It is assumed that segments are chosen in such a way that they have the same volume as the liquid molecules (V_o). Hence, the volume fractions of the liquid (v_1) and the segments are:

$$v_1 = \frac{n}{n + x N}, \quad \text{and} \quad v_2 = \frac{xN}{n + x N}. \tag{2.51}$$

Gibbs potential of mixing ΔG_m is then given as:

$$\Delta G_m = kT[n \ln v_1 + N \ln v_2 + \bar{\alpha} n v_2] \tag{2.52}$$

Here, $\bar{\alpha}$ is the parameter characterizing the interaction energy per liquid molecule ($kT\bar{\alpha}$ represents the difference in energy of a solvent molecule in pure polymer ($v_2 = 1$) compared with one surrounded by molecules of its own kind, i.e., pure liquid).

If m_1 is the mass of liquid molecule and m_2 is the mass of a segment then the total mass of the liquid in the system is:

$$M_1 = nm_1 \tag{2.53}$$

and the total mass of the polymer is:

$$M_2 = x N m_2 \tag{2.54}$$

Consequently, for a unit mass one can write:

$$n_1 = \frac{n}{M}, \quad n_2 = \frac{xN}{M}, \quad M = M_1 + M_2 \tag{2.55}$$

and mass concentrations are:

$$c_1 = n_1 m_1 = \frac{nm_1}{nm_1 + x\,Nm_2} \tag{2.56}$$

$$c_2 = n_2 m_2 = \frac{xNm_2}{nm_1 + xNm_2} \tag{2.57}$$

With the help of these relations one can also write:

$$v_1 = \frac{1}{1 + \frac{m_1}{m_2}\left(\frac{1}{c_1} - 1\right)} \tag{2.58}$$

and

$$v_2 = \frac{1}{1 + \frac{m_2}{m_1}\frac{c_1}{1 - c_1}} \tag{2.59}$$

Since $nm_1 = c_1 M$, then:

$$nm_1 = \frac{c_1}{1 - c_1} M_2 \tag{2.60}$$

and for the density of the system (ρ) we have:

$$\rho = v_1 \frac{m_1}{V_o} + v_2 \frac{m_2}{V_o} \qquad (2.61)$$

Now, for the Gibbs potential (g) of one gram of the mixture one can write:

$$g = \mu c_1$$

where μ is given by Equation (2.20).

Using Equations (2.50) and (2.56), the last equation yields:

$$\mu = \frac{kT}{M_2} \frac{(1 - C_1)}{C_1} [n \ln v_1 + N \ln v_2 + \bar{\alpha} n v_2] \qquad (2.62)$$

It is necessary to consider also the configurational entropy of the network. Assume that we have a unit cube of polymer. Due to the absorption of penetrant, this cube expands homogeneously. The new (swollen) cube has edge lengths λ. Then, $v_2 = 1/\lambda^3$, i.e., $\lambda = v_2^{-1/3}$ and if there is no change of volume on mixing one can write:

$$\lambda^3 = 1 + n V_o \qquad (2.63)$$

Wall and Flory [1951] calculated the entropy of deformation on swelling as follows:

$$\Delta S_{sw} = -\frac{3}{2} N k v_2^{-2/3} [v_2^{-2/3} - 1 - \frac{1}{3} \ln v_2^{-1}] \qquad (2.64)$$

If the enthalpy change on swelling is negligible one can write:

$$\Delta G_{sw} = - T \Delta S_{sw}$$

and using Equation (2.52) one obtains:

$$\mu_{tot} = \frac{kT\ (1 - c_1)}{\overline{M}_2 \quad c_1} [n \ln v_1 + N \ln v_2 + \bar{\alpha} n v_2 +$$

$$\frac{3}{2} N v_2^{-2/3} (v_2^{-2/3} - 1 - \frac{1}{3} \ln v_2^{-1})] \qquad (2.65)$$

Using the definition of the diffusion coefficient D_1 (c.f. Equation 2.41), one can write for the system, swollen polymer + diffusant:

$$D = \frac{\alpha}{\bar{\rho}} \left(\frac{\partial \mu_{tot}}{\partial c_1} \right)_{P,T} \qquad (2.66)$$

Using Equations (2.65) and (2.66), one obtains:

$$D = \frac{\alpha k T N}{M_2 c_1^{\ 2} \left(v_1 \frac{m_1}{\overline{V}_o} + v_2 \frac{m_2}{\overline{V}_o} \right)} \left[-\left(1 + \frac{3}{2} v_2^{-5/3} \left(1 + \frac{v_2}{3}\right)\right) \ln v_2 \right.$$

$$\left. - \frac{M_2}{\overline{M}_1} \frac{c_1 (1 + c_1)}{N} (\alpha v_2 + \ln v_1) + \frac{m_1}{m_2} \frac{(c_1 - 1)}{c_1} v_1^{-2} v_1^{-1} \right.$$

$$+ \frac{M_2}{N} (v_1^{-3} - \alpha v_1^{-2}) + \frac{3}{2} v_2^{-4/3}(v_2^{2/3} - 1)$$

$$+ \frac{3}{2} \frac{m_1}{m_2} v_1^{-2} v_2^{-7/3} (\frac{4}{3} + v_2^{2/3})] \qquad (2.67)$$

With the help of Equations (2.58) and (2.59) one can eliminate the mass concentrations c_1 and c_2 and express D in volume fractions only. Of course, this expression contains also molecular characteristics of both phases of the system ($N_1 m_1$, m_2 and V_o) and the interaction parameter $\bar{\alpha}$.

2.4 Dependence of Diffusion Coefficients on Concentration

It is known that the diffusion coefficient of many easily condensable vapours in elastomers differs from that of most gases in that it is concentration dependent. This is generally caused by swelling which leads to a loosening of the elastomer structure which facilitates the movement of the diffusing molecules. In a highly swollen elastomer, diffusion of the penetrant causing the swelling may even resemble self-diffusion.

The mathematical and experimental approach to concentration-dependent diffusion is very difficult. Usually, in experiments, the vapour pressure of the penetrant is reduced so much that diffusion is no longer concentration dependent. The question remains what happens under other conditions?

Crank and coworkers [Crank and Park, 1968] have developed the

mathematical treatment of a concentration-dependent diffusion coefficient and methods for its experimental determination. The subject has been reviewed by Fujita [1961]. The general diffusion equation has the following form:

$$\frac{\partial c}{\partial t} = \text{div}(D \text{ grad } c) \qquad (2.68)$$

Experimentally, the problem can be approached similarly as the constant diffusion problems. Usually it is assumed that D depends in a simple way on concentration, e.g.,

$$D = D_o e^{a_o c} \quad , \quad \text{or}$$

$$D = D_o(1 + a_1 c + a_2 c^2 + a_3 c^3 + \dots) \quad , \quad \text{or}$$

$$D = D_o(1 + a_c c) \qquad (2.69)$$

According to Crank [1975], in deriving expressions for calculating D, it is possible to assume that the dimensions of the sample remain constant. If swelling causes concentration dependence of the diffusion coefficient, the classical mathematical expressions can still be used provided a frame of reference is taken with respect to the substance of the polymer. In one method, the unit of length is defined as the mass of sample per unit area, i.e., initial length multiplied by density of the polymer. Concentration is defined as the

mass of absorbed substance per unit mass of polymer. The diffusion coefficient then has the dimension $[L^2t^{-1}]$ and will therefore also include a (density)^2 factor. It is more convenient to define the unit length by the unit volume of elastomer without penetrant per unit area [Hartley and Crank, 1949]. This implies that the thickness of a swollen sample measured in this unit is constant and equal to the original unswollen thickness. Concentration is defined as the amount of absorbed substance per unit volume of sample without penetrant. Similarly, the diffusion coefficient refers to diffusion relative to stationary material.

The diffusion coefficient, D_v, expressed in terms of a swollen material is related to the diffusion coefficient, D, as:

$$D_v = \frac{D}{v_2^2} \tag{2.70}$$

where v_2 is the volume fraction of elastomer.

Another useful coefficient of diffusion is the intrinsic diffusion coefficient, D_i. This coefficient is used to correct not only for swelling but also for mass flow. D_i is useful for the molecular interpretation of diffusion. It is defined in terms of rate of transfer across a section fixed so that no mass flow occurs through it [Crank, 1975]. In this case, D_i, is related to D as follows:

$$D_i = D/v_2^2 \tag{2.71}$$

A rapid method for establishing whether a diffusion coefficient is concentration dependent or not is the determination of both absorption and desorption-time curves. These curves would coincide for a constant D, but differ for a concentration dependent diffusion coefficient. The shape of the curves depends on the applied concentration of penetrant. Generally, the shape of the desorption-time curve is more strongly affected by a concentration dependence of D than the absorption-time curve. Moreover, absorption is usually more rapid than desorption [Crank and Henry, 1949].

It should be noticed that time-dependent relaxation processes caused by swelling of the polymer could be very disturbing. Hence, D is not only concentration dependent but also time dependent [Cohen, 1983]. These time effects are particularly apparent for diffusion in polymers below the glass transition temperature. However, similar effects have been found for example in the system benzene-natural rubber [Barrer and Fergusson, 1958].

2.5 Elastomers

2.5.1 Rubber elasticity-viscoelasticity

In macromolecular solids, one has to distinguish between the micro-Brownian motion (movement of chain segments) and the macro-Brownian motion (the movement of entire coils). In the glassy state both types of molecular motion are "frozen". On increasing the temperature the segments of the chain begin to "melt". In the neighborhood of the softening point the free chain segments become larger and larger. Under the influence of a deforming force the

sample slowly changes its shape. The temperature at which deformation occurs depends on the magnitude of such a deforming force.

Further increases in temperature cause the chain segments to become more and more mobile. Finally, for each chain there remain only a few linkage points. The energy required to "melt" a structural unit or a chain segment is always the same. Therefore, the links which still remain at a certain temperature must be distributed at random over the entire material, and there will be a temperature at which each macomolecule is linked to its neighbors only be relatively few valence forces. In this state a considerable deformation is possible even with a relatively small deformation force. However, if the deformation occurs rapidly and does not continue for very long it will not give rise to a movement of the macromolecular coils with respect to each other but only to a deformation of coils. In this process the coils are forced into an improbable shape and the entropy of the system decreases. After removing the deforming force, the coils again return to their most probable form, which results in a return to the original state. The described behavior, i.e. strong deformation under small deforming force and elastic recovery is known as rubber-elasticity or viscoelasticity. A material with this behavior is characterized as "rubbery" or rubber.

Rubber-elasticity is a property which all macromolecular compounds have above their softening (glass) temperature (as long as they do not first decompose). The elasticity of polymers above their glass temperature is not a pure elasticity. For example, after

stretching and releasing the sample, the rubber elastic polymer is always somewhat longer than before stretching. The remaining deformation is larger, the larger the degree of stretching and the longer the sample is held in the deformed state. Thus, if the time of stretching is longer, the stretched molecules have time to change their position with respect to each other, i.e., in their new position they can again attain their most probable shape. The inner tension of the system is relieved by changes in the position of molecules - this process is called relaxation and is characteristic for liquids in flow. Hence, we can consider rubber-elastic melts as liquids with an extremely long relaxation time. On increasing the temperature the liquid-type behavior becomes more and more pronounced. Polymers with softening (glass) temperature below the room temperature, i.e., polymers which at ordinary temperatures are rubber-elastic are known as elastomers. In all elastomers it is possible to change the modulus of elasticity and the maximum deformation by changing the degree of cross-linking.

Historically, the first step for the correct interpretation of rubber elasticity was made when chemists compared the rubber-elastic deformation to the compression of gases. The recovery force of a stretched rubber becomes larger on heating, just as the recovery force of a compressed gas becomes higher on heating. This means that the driving force in the contraction of stretched rubber is not the tendency for the reduction of the internal energy, but the tendency to increase the entropy, just as in gases. The entropy decrease on stretching corresponds to the transition from the most probable coil

structure of the chain to the improbable state of the stretched chains and the entropy increase on recovery corresponds to the return from the improbable oriented chain structure to the more probable statistical coiling after release of the tension. The higher the temperature, the greater the chain mobility, and the larger the entropy loss in the transition to the stretched state where the mobility of the chains is strongly reduced. The greater $T \Delta S$, the greater will be the driving force for the return to the statistically coiled state, and therefore, the stress must increase on heating.

Basic mechanical properties of elastomers can be demonstrated easily on the elongational deformation.

For ideal solids we have Hooke's law:

$$\tau = E \epsilon \tag{2.72}$$

where τ is the unidirectional stress and ϵ is the relative deformation (elongation). E is the elasticity modulus. The behavior of the ideal liquid is described by Newton's law:

$$\tau = \eta_o \dot{\epsilon} \tag{2.73}$$

where η_o is the constant viscosity.

A real rubber-elastic solid is an intermediate between solid and liquid. For short deformation times and small deformations the solid is elastic, but on longer deformation times it starts to flow.

Then we have a viscoelastic solid.

Differentiating Equation (2.72) with respect to time t, one can superpose this equation with Equation (2.73), i.e.,

$$\frac{d\varepsilon}{dt} = \frac{1}{\eta_o}\tau + \frac{1}{E}\frac{d\tau}{dt} \quad (2.74)$$

On integrating Equation (2.74):

$$\tau = \varepsilon_o E e^{-(E/\eta_o)t} = \varepsilon_o E e^{-t/\lambda} \quad (2.75)$$

Here, $\lambda = E/\eta_o$ is the relaxation time. The last equation represents the trivial form of the Maxwell model [Maxwell, 1887].

Viscoelastic deformation is a relaxation in the sense of solid state physics, because it deals with a flow process. However, this flow process involves only molecular groups and segments within one molecule, not the coils themselves. The intramolecular flow process stops itself due to the existence of a counterforce determined by the decrease in entropy which is connected with the flow process. Since this entropy decrease is caused by the deformation of the statistical coil, viscoelasticity is associated with the presence of macromolecules. The chain segments between junctions have to be long enough in order to form coils in the sense of random walk statistics. On increasing temperature, the entropy difference between the elongated state of the deformed coils and their statistically most probable form becomes larger and larger. Since this entropy

difference is the driving force for viscoelastic return motion, the stress of a stretched elastomer increases on heating just as the pressure of a gas increases on heating.

2.6 The Simple Molecular Network Theory

Consider a pure homogeneous strained piece of elastomer, i.e., the strain characterized by three principal extension ratios along three mutually perpendicular axes. Under such a strain a unit cube is transformed into a rectangular parallelelopiped with three unequal edge lengths. These edge lengths are equal to the principal extension ratios λ_1, λ_2 and λ_3 by which the state of pure homogeneous strain in an initially isotropic material is completely specified. Let us assume that the elastomer contains a total of N chains per unit volume of various contour lengths. Each chain is characterized by a value of the parameter β', which depends on its contour length. Let us divide the set of chains into a number of groups, such that the value of chain contour length, i.e., also the parameter β', is the same (with possibly small deviations) for all the members of each group. The total entropy of deformation for the whole ensemble of chains may be obtained as the sum of the entropies for all the chains in every group and then summing over all groups. Let us consider an individual chain with end-to-end distance vector $\underset{\sim}{R} = (x,y,z)$, in the unstrained state of the network. Under the assumption of affine deformations, this chain after deformation has the end-to-end vector

$\underset{\sim}{R} = (x', y', z')$ where:

$$x' = \lambda_1 x, \quad y' = \lambda_2 y, \quad z' = \lambda_3 z \tag{2.76}$$

The coordinate system coincides with the principal axes of strain.

Assuming that the chain is of the Gaussian type [Khun, 1934], i.e., the entropy of the chain may be represented by the formula:

$$S = c' - k\beta'^2(x^2 + y^2 + z^2) \tag{2.77}$$

where k is the Boltzmann constant. The corresponding entropy after deformation is then:

$$S' = c' - k\beta'^2(\lambda_1^2 x^2 + \lambda_2^2 y^2 + \lambda_3^2 z^2) \tag{2.78}$$

The contribution to the total entropy of deformation is given as:

$$\Delta S = S'-S = -k\beta'^2[(\lambda_1^2-1)x^2 + (\lambda_2^2-1)y^2 + (\lambda_3^2-1)z^2] \tag{2.79}$$

In a group of - n chains, characterized by the parameter ν'_n and a number of chains N_n we have:

$$\Delta S_n = \sum_{i=1}^{N_n} \Delta S_{in} = -k\beta_n'^2[(\lambda_1^2 - 1)\sum_i x_{in}^2 + (\lambda_2^2 - 1)\sum_i y_{in}^2 +$$

$$+ (\lambda_3^2 - 1)\sum_i z_{in}^2] \qquad (2.80)$$

For a random network in the undeformed state all directions of $\underset{\sim}{R}$-vectors are equally probable - this holds for any subgroup as well as for the whole ensemble. Since:

$$\sum x^2 + \sum y^2 + \sum z^2 = \sum |\underset{\sim}{R}|^2$$

one can write:

$$\sum_i x_{in}^2 = \sum_i y_{in}^2 = \sum_i z_{in}^2 = \frac{1}{3}\sum_i R_{in}^2 \qquad (2.81)$$

Moreover,

$$\sum_i R_{in}^2 = N_n \langle R_{in} \rangle^2 \qquad (2.82)$$

where $\langle R_{in} \rangle^2$ is the mean-square vector length for this group of chains. Using Equations (2.81) and (2.82) the entropy of deformation for this group is:

$$\Delta S_n = -\frac{1}{3} k N_n \beta_n'^2 \langle R_{in} \rangle^2 (\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \qquad (2.83)$$

For Gaussian chains one also has the known relation [Treolar, 1958]:

$$\langle R_{in} \rangle^2 = \frac{3}{2} \beta_n'^2 \qquad (2.84)$$

Denoting $\sum N_n = N$ and using Equation (2.84), one can write for the total entropy of deformation:

$$\Delta s = \sum_n \Delta s_n = -\frac{1}{2} Nk(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \qquad (2.85)$$

Introducing the usual assumption that there is no change in the internal energy of the system on deformation, one can evaluate the Helmholtz free energy (A) with the help of Equation (2.81). Since $A = -T\Delta s$, we have:

$$A = \frac{1}{2} NkT (\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \qquad (2.86)$$

This is the expression for the work of deformation or elastic stored free energy (simply stored-energy function) per unit volume of the elastomer. Usually this expression is written as:

$$A = \frac{1}{2} G(\lambda_1^2 + \lambda_2^2 + \lambda_3^2) \qquad (2.87)$$

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where the modulus G is given by:

$$G = NkT \tag{2.88}$$

The quantity N (number of chains per unit volume) is determined by the degree of cross-linking, hence N (and also G) may be expressed in terms of the number average chain molecular weight $\bar{M}_n$:

$$G = NkT = \rho RT/\bar{M}_n \tag{2.89}$$

where ρ is the density of the material and R is the universal gas constant.

2.7 Swelling

Consider the elastic properties of a swollen elastomer from the point of view of elementary network theory.

Assume again that the elastomer in the unswollen state has the form of a unit cube, and that it contains N chains per unit volume. The degree of swelling can be defined by the volume fraction v of polymer in the mixture of polymer and liquid. The volume swelling ratio is then given by $\frac{1}{v}$ and the length of the edge of the cube in the unstressed state is $\lambda_o = 1/3 \sqrt{v}$. Let the original unit cube be swollen in the ratio 1/v, i.e., deformed to dimensions ℓ_1, ℓ_2 and ℓ_3 by the principal stresses. The total change in the network entropy ($\Delta S'_o$) in passing from the unstrained unswollen state to the strained swollen state is given by Equation (2.85), i.e.,

$$\Delta S_o' = -\frac{1}{2} Nk(\ell_1^2 + \ell_2^2 + \ell_3^2 - 3) \qquad (2.90)$$

The change in entropy (ΔS_o) due to the isotropic swelling in the ratio $\lambda_o = 1/3 \sqrt{v}$ in the absence of stress is:

$$\Delta S_o = -\frac{1}{2} Nk(3\lambda_o^2 - 3) = -\frac{1}{2} Nk(3v^{-2/3} - 3) \qquad (2.91)$$

Then the required entropy of deformation of the swollen network ($\Delta S'$) is:

$$\Delta S' = \Delta S_o' - \Delta S_o = -\frac{1}{2} Nk(\ell_1^2 + \ell_2^2 + \ell_3^2 - 3v^{-2/3}) \qquad (2.92)$$

Writing $\ell_1 = \lambda_1/v^{1/3}$, $\ell_2 = \lambda_2/v^{1/3}$ and $\ell_3 = \lambda_3/v^{1/3}$ (referred to the swollen unstrained state) the last equation can be written as:

$$\Delta S' = -\frac{1}{2} Nk\, v^{-2/3} (\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \qquad (2.93)$$

This is the entropy of deformation per unit volume, measured in the unswollen state. To obtain the stored-energy function per unit volume we need the entropy of deformation per unit volume, measured in the swollen state. Denoting this by ΔS, we have:

$$\Delta S = v\Delta S' = -\frac{1}{2} Nkv^{1/2}(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \qquad (2.94)$$

The corresponding stored-energy function (W) is then:

$$A = W = -T\Delta S = \frac{1}{2} NkT\, v^{1/3}(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \qquad (2.95)$$

The only difference between Equation (2.95) and the case of unswollen elastomer is the factor $v^{1/3}$ in the modulus. Then, if G and G' are the respective moduli in the unswollen and in the swollen states, we can write:

$$G' = G\, v^{1/3} = \frac{\rho RT}{\bar{M}_n} v^{1/3} \qquad (2.96)$$

Let us note that Flory [1951] proposed a modified (and more precise) expression for $\Delta S'_o$:

$$\Delta S'_o = -\frac{1}{3} Nk[\ell_1^2 + \ell_2^2 + \ell_3^2 - 3 \ln(\ell_1\ell_2\ell_3)] \qquad (2.97)$$

In swelling, we are concerned with the equilibrium between phases. The mixed phase is solid and the pure phase is liquid. The equilibrium is determined by the condition that the free energy is minimum with respect to changes in composition of phases. In our case when the mixed phase is polymer + liquid and the single phase is pure liquid this means that the change in free energy on transferring a small quantity of liquid from the pure liquid phase to the mixed phase must be zero. One can introduce the Gibbs free energy (Gibbs potential) of dilution ΔG_1, defined as the change in Gibbs potential of the system resulting from the transfer of a unit quantity of liquid

from liquid phase to a very large quantity of the mixture. For a system maintained at constant pressure the condition for equilibrium with respect to the transfer of liquid is then:

$$\Delta G_1 = 0 \qquad (2.98)$$

Using the enthalpy of dilution ΔH_1 and the entropy of dilution ΔS_1 we can write:

$$\Delta G_1 = \Delta H_1 - T\Delta S_1 \qquad (2.99)$$

Here, ΔH_1 and ΔS_1 are the changes in heat content (H) and entropy (S) of the system due to the transfer of one mole of liquid from the liquid phase to a large quantity of the mixed phase. Since,

$$H = U + PV \qquad (2.100)$$

where P is the pressure applied, U is the internal energy, V is the volume and since under normal conditions PV may be neglected, H and U are practically equivalent.

In the case when only one component (the low molecular penetrant) has an appreciable vapour pressure, the Gibbs potential of dilution is given as [Treolar, 1958]:

$$\Delta G_1 = RT \ln(P/P_o) \qquad (2.101)$$

Here P is the vapour pressure of liquid in equilibrium with the mixture at temperatur T and P_o is its saturation pressure (assuming that vapour is a perfect gas).

The essential process in swelling is the diffusion of the liquid molecules into the polymer. In elastomers this process takes place with an increase in entropy but with negligible change in internal energy. The increase in entropy arises from the greater probability of the mixed state compared with the unmixed state, and may be in principle calculated in terms of the number of configurations available to the system in any specific state. Very simple methods for the calculation of the configurational entropy of mixing have been developed by Flory [1942] and Huggins [1942].

In Flory's model the liquid and polymer molecules are arranged on a three-dimensional lattice of sites such that each site may be occupied either by a liquid molecule or by a single segment of a polymer chain. The entropy of dilution (ΔS_1) with respect to the liquid component, in terms of molar quantities, is given as:

$$\Delta S_1 = - R[\ln(1-v_1) + (1 - \frac{1}{x})v_2] \qquad (2.102)$$

where x is the number of segments in the polymer molecule, v_1 and v_2 are the respective volume fractions of liquid and polymer in the mixture.

Using a more precise analysis of the number of sites available to

the segments of the polymer molecule Huggins obtained:

$$\Delta S_1 = -R[\ln(1-v_2) - \frac{Z}{2}(1 - \frac{1}{x})\ln(1 - \frac{2v_2}{Z})] \qquad (2.103)$$

where Z is the number of nearest-neighbor sites to segment of the polymer molecule.

Both methods are formally equivalent and give the following expression for the free energy of dilution (Flory-Huggins equation):

$$\Delta G_1 = RT[\ln(1 - v_2) + v_2 + \bar{\alpha} v_2^2] \qquad (2.104)$$

where $\bar{\alpha}$ is a parameter of the particular polymer-liquid system.

For cross-linked polymers Equation (2.104) is insufficient and one has to account also for the configurational entropy of the network. Writing the total free energy of dilution ΔG_1 as:

$$\Delta G_1 = \Delta G_{1u} + \Delta G_{ie} \qquad (2.105)$$

where ΔG_{1u} is the free energy of dilution for the uncrosslinked polymer and ΔG_{ie} is the free energy change due to the elastic expansion of the network on the absorption of one mole of liquid. The second term can be obtained from the stored-energy function (cf. Equation 2.95). For a simple expansion of a unit cube such that all dimensions are increased in the ratio λ we have;

$$W = \frac{\rho RT}{2\bar{M}_n}(3\lambda^2 - 3) = \frac{3\rho RT}{2\bar{M}_n}(v_2^{-2/3} - 1) \qquad (2.106)$$

where $\lambda^3 = 1/v_2$ is the volume in the swollen state. If n_1 is the number of moles in the system, then:

$$\lambda^3 = 1/v_2 = 1 + n_1 V_1 \qquad (2.107)$$

where V_1 is the molar volume of the liquid. Then,

$$\Delta G_{1e} = \frac{\partial W}{\partial n_1} = \frac{\rho RT}{\bar{M}_n} V_1 v_2^{1/3} \qquad (2.108)$$

Using the Flory-Huggins equation and expression for ΔG_{1u}, one can write:

$$\Delta G_1 = RT[\ln(1 - v_2) + v_2 + \bar{\alpha} v_2^2 + \frac{\rho V_1}{\bar{M}_n} v_2^{1/3}] \qquad (2.109)$$

The condition for equilibrium swelling is then:

$$\ln(1 - v_2) + v_2 + \bar{\alpha} v_2^2 + \frac{\rho V_1}{\bar{M}_n} v_2^{1/3} \qquad (2.110)$$

Using Equation (2.97), one obtains:

$$\Delta G_{1e} = \frac{\rho RT}{\bar{M}_n} V_1 (v_2^{1/3} - \frac{v_2}{2}) \qquad (2.111)$$

and the equilibrium condition is:

$$\ln(1 - v_2) + v_2 + \bar{\alpha} v_2^2 + \frac{\rho V_1}{\bar{M}_n} v_2^{1/3} = 0 \qquad (2.112)$$

Using Equation (2.97), one obtains:

$$\Delta G_{1e} = \frac{\rho RT}{\bar{M}_n} V_1 (v_2^{1/3} - \frac{V_2}{2}) \qquad (2.113)$$

and the equilibrium condition is:

$$\ln(1 - v_2) + v_2 + \bar{\alpha} v_2^2 + \frac{\rho V_1}{\bar{M}_n} (v_2^{1/3} - \frac{v_2}{2}) = 0 \qquad (2.114)$$

It is known that the material absorbs more liquid in the strained state than in the unstrained state [Gee, 1946]. Hence, if one considers a sample of the cross-linked material, originally in the form of a unit cube, which is in contact with a low-molecular liquid and is constrained by forces applied to its faces. The sample will form a rectangular block with dimensions ℓ_1, ℓ_2 and ℓ_3. The edges of the block define the principal axes of the pure homogeneous strain, and the principal stresses τ_I, τ_{II} and τ_{III} will act normally to the

respective surfaces. If the liquid and polymer are assumed to mix without a change of volume, we have:

$$\ell_1\ell_2\ell_3 = 1/v_2 = 1 + n_1V_1 \qquad (2.115)$$

where n_1 is the number of moles of liquid in the polymer, V_1 is the molar volume of the liquid and v_2 is the volume fraction of polymer. As before, we can write:

$$\Delta G = \Delta G_u + \Delta G_e \qquad (2.116)$$

where ΔG is the total change in Gibbs potential of the system in passing from the unstrained unswollen state to the strained swollen state, and ΔG_u and ΔG_e represent the corresponding free energies of mixing and of network extension (total quantities).

Assume that δn_1 moles of liquid are absorbed under the conditions: ℓ_2 = constant, ℓ_3 = constant, and ℓ_1 is increased by $\delta\ell_1$. Since the work is done by τ_I we have for the total work done by external forces:

$$\delta W = \tau_I\ell_2\ell_3\delta\ell_1 = \tau_I V_1\delta n_1 \qquad (2.117)$$

For a small departure from equilibrium we have:

$$\delta\Delta A = \delta W \qquad (2.118)$$

Since $\Delta G = \Delta A + P\Delta V$, and in our case $\Delta V = 0$ we can write:

$$\delta\Delta G = \delta W = \tau_I V_1 \delta n_1 \tag{2.119}$$

or

$$\left(\frac{\partial \Delta G}{\partial n_1}\right)_{\ell_2 \ell_3} = \tau_I V_1 \tag{2.120}$$

From Equation (2.116), it follows that:

$$\left(\frac{\partial \Delta G}{\partial n_1}\right)_{\ell_2 \ell_3} = \frac{\partial \Delta G_u}{\partial n_1} + \left(\frac{\partial \Delta G_3}{\partial n_1}\right)_{\ell_2 \ell_3} \tag{2.121}$$

The first term on the right side is given by the Flory-Huggins relation (cf. Equation 2.104), i.e.:

$$\frac{\partial \Delta G_u}{\partial n_1} = RT[\ln(1 - v_2) + v_2 + \bar{\alpha} v_2^2] \tag{2.122}$$

For the stored-energy function in a swollen material, we applyEquations (2.86) and (2.89), i.e.:

$$\Delta G_e = W = \frac{\rho RT}{\bar{M}_n}(\ell_1^2 + \ell_2^2 + \ell_3^2 - 3) \tag{2.123}$$

which in combination with Equation (2.122) gives:

$$\left(\frac{\partial \Delta G_e}{\partial n_1}\right)_{\ell_2 \ell_3} = \left(\frac{\partial \Delta G_e}{\partial \ell_1}\right)\left(\frac{\partial \ell_1}{\partial n_1}\right)_{\ell_2 \ell_3} = \frac{\rho V_1 RT}{\bar{M}_n} v_2 \ell_1^2 \qquad (2.124)$$

Finally, using Equations (2.124) and (2.120), one obtains:

$$\tau_I = \frac{RT}{\bar{V}_1}\left[\ln(1 - v_2) + v_2 + \bar{\alpha} v_2^2 + \frac{\rho V_1}{\bar{M}_n} v_2 \ell_1^2\right] \qquad (2.125)$$

Similar equations hold for τ_{II} and τ_{III}. From these equations one can obtain three equations of the type:

$$\tau_I - \tau_{II} = \frac{\rho RT}{\bar{M}_n} v_2(\ell_1^2 - \ell_2^2) = \frac{\rho RT}{\bar{M}_n} v_2^{1/3} (\lambda_1^2 - \lambda_2^2) \qquad (2.126)$$

where λ_1, λ_2 and λ_3 are the principal extension ratios with respect to the swollen unstrained state. We can see that the stresses are indetermined (an isotropic pressure can be superimposed) - only the difference of stresses is given.

The following special problems have been solved by Treolar [1953].

1. Isotropic pressure:

A hydrostatic pressure P is applied to the swollen material; then

$$\tau_I = \tau_{II} = \tau_{III} = P, \qquad \ell_1 = \ell_2 = \ell_3 = v_2^{-1/3}$$

Equation (2.125) then yields:

$$-P = \frac{RT}{\bar{V}_1}\left[\ln(1 - v_2) + v_2 + \bar{\alpha} v_2^2 + \frac{\rho V_1}{\bar{M}_n} v_2^{1/3}\right] \qquad (2.127)$$

2. Simple elongation:

For a tensile stress τ_I (acting in the direction ℓ_1):

$$\tau_{II} = \tau_{III} = 0, \qquad \ell_2^2 = \ell_3^2 = 1/\ell_1 v_2$$

and the equivalent of Equation (2.125) gives the equilibrium condition:

$$\tau_{II} = \frac{RT}{\bar{V}_1}\left[\ln(1 - v_2) + v_2 + \bar{\alpha} v_2^2 + \frac{\rho V_1}{\bar{M}_n \ell_1}\right] = 0 \qquad (2.128)$$

3. Uniform two-dimensional extension

Here,

$$\tau_I \; 0, \quad \tau_{II} = \tau_{III} \quad \text{and} \quad \ell_2^2 = \ell_3^2 = 1/\ell_1 v_2$$

then

$$\tau_I = \frac{RT}{V_1}\left[\ln(1 - v_2) + v_2 + \bar{\alpha} v_2^2 + \frac{\rho V_1}{\bar{M}_n v_2 \ell_2^4}\right] = 0 \qquad (2.129)$$

Here, ℓ_2 is the stretch ratio in the plane of the stretched sheet with respect to the unswollen unstrained dimensions.

3. EXPERIMENTAL

3.1 General

In an earlier report [Asfour et al. 1986], we developed an expression for calculating the diffusion coefficient at zero penetrant concentration in a thin polymer sheet using the desorption technique. The rubber samples received from DREO for the current contract provide rectangular parallelepipeds and not thin sheets. This requires a different mathematical treatment. The details of this treatment are described below.

3.2 Desorption from a Rectangular Parallelepiped

Assume that the sample is in the form of a rectangular parallelepiped and is immersed in a test tube containing the penetrant under investigation. The system is kept in a bath at constant temperature. After sufficiently long time the equilibrium state is reached. The sample is then suspended on the balance, the vacuum system is operated and the desorption kinetics are followed by monitoring the weight loss with time [Asfour et al. 1986].

In Cartesian coordinates (x,y,z) the sample is defined as the domain:

$$\{\underset{\sim}{x};\ \underset{\sim}{x} \in V = (o,\bar{a}) \times (o,\bar{b}) \times (o,\bar{c});\ x = (\underset{\sim}{x},y,z)\} \qquad (3.1)$$

and the desorption experiment can be mathematically described as follows:

$$\frac{\partial c}{\partial t} = \Delta c, \quad c \equiv c(x,y,z,t) \tag{3.2}$$

$$c = c_o \text{ at } t = 0 \text{ for } \underset{\sim}{x} \in V$$

$$c = 0 \text{ at } t > 0 \text{ for } \underset{\sim}{x} \in \partial V \tag{3.3}$$

$$c \to 0 \text{ for } t \to \infty \text{ and } \underset{\sim}{x} \in V$$

Here, D is the constant diffusion coefficient, c_o is the equilibrium concentration in the sample and ∂V is the boundary (surface) of V.

Using the method of separation of variables one can easily obtain the following series solution:

$$c = \frac{64\, c_o}{\pi^3} \sum_{m,n,r=0}^{\infty} \frac{1}{(2m+1)(2n+1)(2r+1)} \sin \frac{(2m+1)\pi X}{\bar{a}}$$

$$\sin \frac{(2n+1)\pi y}{\bar{b}} \sin \frac{(2r+1)\pi z}{\bar{c}}\, e^{-\pi^2 D[(\frac{2m+1}{\bar{a}})^2 + (\frac{2n+1}{\bar{b}})^2 +}$$

$$(2r+1)^2]t \tag{3.4}$$

Knowing the concentration $c(\underset{\sim}{x},t)$ one can calculate the total amount of penetrant desorbed at any time (Q_t):

$$Q_t = \int_0^t \int_{\partial V} - D\nabla c \cdot \underset{\sim}{n}\, d\sigma\, dt' = - D \int_0^t \int_V \Delta c\, dV\, dt$$

$$= \int_V (c - c_o)dV \qquad (3.5)$$

where $\underset{\sim}{n}$ is the outward unit normal. Gauss's theorem has been used in the last transformation.

Substituting c, given by Equation (3.4) into Equation (3.5), one can write:

$$Q_t = Q_\infty - \frac{512}{\pi^6} Q_\infty \sum_{m,r,r=0}^{\infty} \frac{e^{-\pi^2 D[(\frac{2m+1}{\bar{a}})^2 + (\frac{2n+1}{\bar{b}})^2 + (\frac{2r+1}{\bar{c}})^2]t}}{(2m+1)^2(2n+1)^2(2r+1)^2} \qquad (3.6)$$

where

$$Q_\infty = -(\bar{a}\,\bar{b}\,\bar{c})c_o \qquad (3.7)$$

If M_t denotes the weight of the dry sample plus the weight of penetrant at time t, then:

$$M_t - M_\infty = Q_\infty - Q_t = \frac{512}{\pi^6} Q_\infty \sum_{m,n,r=0}^{\infty} \frac{e^{-\pi^2 D[(\frac{2m+1}{\bar{a}})^2 + (\frac{2n+1}{\bar{b}})^2 + (\frac{2r+1}{\bar{c}})^2]t}}{(2m+1)^2(2n+1)^2(2r+1)^2} \tag{3.8}$$

After a sufficiently long time interval one can take only the first term in series given by Equation (3.8) and write:

$$\frac{d}{dt}(\ln(M_t - M_\infty)) = -\pi^2 D_o \left(\frac{1}{\bar{a}^2} + \frac{1}{\bar{b}^2} + \frac{1}{\bar{c}^2}\right) \tag{3.9}$$

or denoting

$$k = \frac{d \ln(M_t - M_\infty)}{dt} \tag{3.10}$$

Then one can write:

$$D_o = -\frac{k(\bar{a}\,\bar{b}\,\bar{c})^2}{\pi^2[(\bar{a}\,\bar{b})^2 + (\bar{a}\,\bar{c})^2 + (\bar{b}\,\bar{c})^2]} \tag{3.11}$$

Of course, if the sample has the form of a sheet, i.e., the thickness ℓ is much smaller than the other dimensions, then the last equation yields:

$$D_o = -\frac{k\,\ell^2}{\pi^2} \tag{3.12}$$

This result has been used in a previous report [Asfour et al. 1986] for calculating the diffusivities in Low Density Polyethylene (LDPE), Natural Rubber (NR) and Bromobutyl Rubber (BIIR).

3.3 Continuous-Flow Permeation Chamber

Another simple method for determining the diffusivity is the method of step concentration change in a continuous-flow permeation chamber [Pasternak et al. 1970; Felder et al. 1974].

A continuous-flow permeation chamber consists of two compartments separated by a membrane. At the time t=0, a penetrant is introduced into the upstream compartment. This penetrant is allowed to permeate through the membrane into a downstream compartment with a stream flowing through. The concentration of the penetrant in the gas leaving the downstream compartment is monitored continuously until the steady-state is obtained. It is assumed that diffusion of the penetrant in the gas phase and absorption at the membrane surface are instantaneous processes. Furthermore, it is assumed that diffusion in the membrane is Fickian and that the concentration of the dissolved gas at the downstream surface of the membrane is sufficiently low with respect to the concentration at the upstream surface, i.e., it may be set to zero. The diffusion equation and boundary conditions for a flat membrane of thickness ℓ are:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}, \quad c \equiv c(x,t) \tag{3.13}$$

$$c(x,o) = 0,\ c(o,t) = c_1,\ c(\ell,t) = 0 \qquad (3.14)$$

Transforming the nonhomogeneous conditions given by Equation (3.14) into homogeneous conditions and using the separation of variables one can easily find the concentration c(x,t):

$$c(x,t) = c_1 - \frac{c_1 x\ 2c_1}{\ell\ \pi} \sum_{n=1}^{\infty} \frac{1}{n} e^{-\frac{Dn^2\pi^2}{\ell^2} t} \sin \frac{n\pi}{\ell} x \qquad (3.15)$$

Using Equation (3.15) one can calculate the rate of permeation (R(t)) for a membrane with the surface area σ as follows:

$$R(t) = - D\sigma \frac{\partial c}{\partial x}\Big|_{x=\ell}$$

$$R(t) = R_\infty [1 + 2 \sum_{n=1}^{\infty} (-1)^n e^{- D \frac{D^2\pi^2}{\ell^2} t}] \qquad (3.16)$$

where $R_\infty = \frac{D\sigma c}{\ell}$ is the steady permeation rate.

The total amount (Q_t) of the penetrant that has permeated through the membrane (at the time t) is then:

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$$Q_t = \int_o^t R(t)dt =$$

$$= R_\infty t + 2R_\infty \sum_{n=1}^{\infty} \frac{(-1)^n \ell^2}{Dn^2\pi^2} - 2 R_\infty \sum_{n=1}^{\infty} \frac{(-1)^n \ell^2}{Dn^2\pi^2} e^{-\frac{D_n^2\pi^2}{\ell^2} t} \tag{3.17}$$

Denoting:

$$M_o = \int_o^t [1 - \frac{R(t)}{R_\infty}]dt \tag{3.18}$$

one can integrate Equation (3.16) and write:

$$M_o = \frac{2\ell^2}{D\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n^2} = \frac{\ell^2}{6D} \tag{3.19}$$

or

$$D = \frac{\ell^2}{6 M_o} \tag{3.20}$$

Experimental values of R(t) may be substituted into Equation (3.18) and the value of M_o may be obtained by numerical integration. The diffusivity D is then given by Equation (3.20).

This method requires simple numerical integration and it utilizes the complete response, rather than a portion of the data in asymptotic region of the solution of the diffusion equation.

3.4 Calculation of Diffusivity from Experimental Data

For the diffusivity calculations one can use the equations derived in Section 3.2. Assuming that the sample has the form of a rectangular parallelepiped one can calculate the zero-concentration coefficient $\bar{D}_o$ as follows:

$$\bar{D}_o = -\frac{k}{\pi^2} \frac{(\bar{a}\,\bar{b}\,\bar{c})^2}{[(\bar{a}\,\bar{b})^2 + (\bar{a}\,\bar{c})^2 + (\bar{b}\,\bar{c})^2]} \qquad (3.19)$$

where $\bar{a}$, $\bar{b}$ and $\bar{c}$ are dimensions of the sample and k is given by Equation 3.10. Asfour et al. [1986] measured the diffusivity for samples with $\bar{a} \gg \bar{c}$ and $\bar{b} \gg \bar{c}$. Then the diffusivity can be calculated via the reduced form of Equation (3.19), i.e.,

$$D_o = -\frac{k}{\pi^2} \bar{c}^2 \qquad (3.20)$$

where $\bar{c}$ represents the thickness of the sample.

In our case, the thickness of investigated elastomers ($\bar{c}$) is much greater than for samples investigated in previous report and it is necessary to calculate $\bar{D}_o$. Both diffusivities, $\bar{D}_o$ and D_o can be easily compared. It follows from Equations (3.19) and (3.20) that:

$$\bar{D}_o = D_o + \frac{k}{\pi^2} \sum_{n=1}^{\infty} (-1)^{n+1} \bar{c}^{-2(n+1)} (\bar{a}^{-2} + \bar{b}^{-2})^n \qquad (3.21)$$

Since $k < 0$ one can see that:

$$\bar{D}_o < D_o \tag{3.22}$$

If the dimensions of the sample are known, one can easily calculate the "correction" term in Equation (3.19).

For all studied systems (penetrant-elastomer) swelling has been found. Hence, the diffusion coefficient $\bar{D}_v^o$, expressed in terms of swollen material is also calculated as follows:

$$\bar{D}_v^o = \frac{\bar{D}_o}{v_2^{\frac{1}{3}}} \tag{3.23}$$

where v_2 is the volume fraction of elastomer.

Just for comparison, the intrinsic diffusion coefficient, $\bar{D}_i^o$ is also calculated as follows:

$$\bar{D}_i^o = \frac{\bar{D}_o}{v_2^{\frac{1}{3}}} \tag{3.24}$$

3.5 Experimental Procedure

The experimental apparatus used consists of an electrorecording balance (CAHN 2000), vacuum system, daata acquisition unit (HP 3421A), temperature controller (Sargent-Welch ST Model) and a Unitron 2200

microcomputer with printer.

The apparatus and the basic experimental procedure were described earlier by Asfour et al. [1986]. The only change made in this study is recording the dimensions of the sample (for dry sample, swollen sample and the sample after desorption process). The equilibrium intake of penetrant has been also recorded on a Mettler balance.

Denoting M_{DW} the mass of the dry sample, M_o the mass of the sample in equilibrium swollen state (sample and penetrant), ρ_1 the density of penetrant and ρ_2 the density of elastomer one can calculate the fractional volumes of penetrant (V_1) and elastomer (v_2) as follows:

$$v_2 = \frac{1}{1 + \frac{M_1\rho_2}{M_{DW}\rho_1}} \qquad (3.25)$$

$$v_1 = 1 - v_2$$

where $M_1 = M_o - M_{DW}$

The value of v_2 is then used in calculating $\bar{D}_v^o$ and $\bar{D}_i^o$. All the results reported here, were obtained fronmn the desorption kinetics. In this method, the time dependence of $M_t - M_\infty$ can be plotted. From the asymptotic behavior, the value of the tangent, k, can be determined. All the studied samples were swollen in the used penetrants (some of them considerably), but it has been found that all

of them returned to their original volumes almost completely. Unfortunately, the supplied elastomers have not been accompanied by an appropriate rheological characteristic, hence, it is not possible to calculate all characteristics of swelling, described earlier. All experiments are being performed at constant temperatures, viz., 25°C and no attempt was made to determine the temperature dependency of $\bar{D}_o$ or other diffusion coefficients.

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